# Vibrational Fine Structure in the Electronic Spectrum of Planar $CuCl_4^{2-}$

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*Summary* Vibrational progressions of frequency 265 ± 20 $cm^{-1}$ probably in the $a_{1g}$ mode have been observed at 77 K on two of the three *d–d* transitions of the planar anion present in (*N*-methylphenethylammonium)$_2$CuCl$_4$.

WHILE vibrational fine structure is observed only rarely in spin-allowed *d–d* transitions such detail is valuable because it provides direct information on the vibronic intensity mechanism, and on the potential energy surfaces of the excited electronic states and the way in which these are related to electronic absorption spectra.[1,2] We have recently measured the spectrum of the (010) face of crystals of (*N*-methylphenethylammonium)$_2$CuCl$_4$, (I), which contains discrete, centrosymmetric, planar $CuCl_4^{2-}$ ions (Cu–Cl bond distances 224·4 and 228·1 pm).[3] Below *ca.* 100 K each of the three peaks comprising the spectrum exhibits fine structure (Figure); for the two outside peaks this is well resolved and the components have a regular spacing of 265 ± 20 $cm^{-1}$. The most reasonable explanation for this is that at low temperatures each major band is predominantly due to a transition from the 0 vibrational states of the ground electronic state to an excited electronic state plus 1 quantum of the appropriate *u*-vibrational mode and with the additional excitation of a number of quanta of the $a_{1g}$ mode of the excited electronic state. A similar effect was reported for an electronic transition of $PtCl_4^{2-}$ (frequency = 280 $cm^{-1}$).[4] The Raman spectrum of (I) suggests a frequency of 276 $cm^{-1}$ for the $a_{1g}$ mode in the ground electronic state.

The progressional frequencies in (I), and the fact that these are regular and observed on each major band, suggest a lengthening of the equilibrium Cu–Cl bond length and a similar slight lowering of the $a_{1g}$ frequency in each excited state (which seems reasonable as promotion occurs to a more strongly antibonding orbital), as well as a low anharmonicity for this mode. The small half-widths (*ca.* 250 $cm^{-1}$) of the individual vibronic transitions, and the fact that spin-allowed *d–d* transitions are generally broad although similar vibronic widths are expected in most metal complexes, suggest that excitations to multiplets of $a_{1g}$ vibrational states are a common feature of *d–d* spectra.[5]

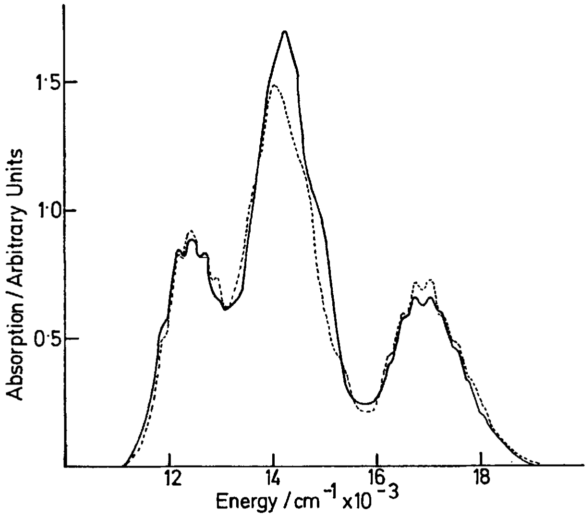

FIGURE. Absorption spectrum at 77 K of the (010) face of (I) with the electric vector along the extinction direction at −84° —— and 6° - - - - to the *a* axis (the − sign indicates rotation away from the obtuse angle).

This implies that attempts to rationalize the variations in intensity and band maximum of such peaks with temperature should always consider changes in the overlap between the vibrational wavefunctions of the ground electronic state and the whole manifold of $a_{1g}$ modes of the excited states. Moreover, the energy of each excited electronic state at its equilibrium nuclear geometry must be at least as low as the onset of each band (*ca.* 1200 $cm^{-1}$ from the peak maximum in the present case). While the maximum overlap between ground and excited state vibrational wavefunctions may well approximately correspond to an excited state energy with a nuclear geometry identical to the ground-state,[2] it seems clear that care must be exercised when excited state energies estimated using ground-state nuclear geometries are equated to electronic spectral band maxima.

The *d*-orbital energy sequence in planar $CuCl_4{}^{2-}$ has been the subject of considerable speculation.[6] The polarization properties of the central peak of (I) are in accordance with its assignment as $A_g\ (x^2 - y^2) \rightarrow B_{1g}\ (xy)$. However, this band also has the most poorly resolved vibrational structure, a characteristic expected for the closely spaced transitions $A_g\ (x^2 - y^2) \rightarrow B_{2g}\ (xz)$, $B_{3g}\ (yz)$. Thus, while the spectra tend to suggest that $d_{xy}$ lies between $d_{z^2}$ and $d_{xz}$, $d_{yz}$ in energy, the matter is not yet proven and we are extending our measurements to lower temperatures and different crystal faces of (I) to try to settle this question.

To our knowledge, this is the first report of vibrational structure in the electronic spectrum of a copper complex, though perhaps studies of other compounds with simple molecular structures and widely spaced electronic transitions may reveal similar detail. Possibly, the anomalous extra peaks sometimes observed[7] in copper spectra may also be due to partially resolved vibrational structure.

(*Received*, 19*th August* 1975; *Com.* 955.)

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